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(54) Liquid cleaning products.

(57) Non-aqueous liquid cleaning product compositions comprise a particulate solid phase dispersed in a non-aqueous liquid phase. The compositions contain a polymer comprising at least one first group capable of association with the particles of the solid phase and at least one second group capable of extending away from the surface of the particles.

EP 0 510 762 A2

The present invention relates to substantially non-aqueous liquid cleaning products, especially detergent compositions containing particulate solid materials. Non-aqueous liquids are those containing little or no water.

In liquid detergents in general, especially those for the washing of fabrics, it is often desired to suspend particulate solids, which have beneficial auxiliary effects in the wash, for example detergency builders to counteract water hardness, as well as bleaches.

EP-A-413 616 discloses non-aqueous liquid detergent compositions comprising nonionic surfactants, solid particles and a polymer derived from α,β-monethylenically unsaturated carboxy-containing monomers.

It is often desired to add one or more ingredients to these systems in order to provide one or more of the following advantages:

(a) to improve the solid suspending properties of the system;
(b) to reduce the clear layer formation upon storage;
(c) to reduce the need of other stabilising materials;
(d) to reduce ashing in fabric washing applications;
(e) to reduce the consistency of the product (as described in H.Barnes, J.F. Hutton, K.Walters "An introduction to Rheology", Elsevier Press 1989);
(f) to provide an increased tolerance for high levels of solid materials in the system;
(g) to improve detergency;
(h) to reduce the setting of the system upon storage.

We have found that improved non-aqueous liquid detergent compositions comprising a dispersed solid phase can be formulated by incorporating therein a specific polymer material. Suitable polymer materials comprise at least one group capable of association with the solid phase and at least one group capable of extending from the solid phase.

Thus according to the invention there is provided a non-aqueous liquid cleaning composition comprising a particulate solid phase which is dispersed in a non-aqueous liquid phase, and a polymer, wherein the polymer is a random or block copolymer having the general formula:

$$A_nB_mC_p$$

wherein:

A is a monomer or a mixture of monomers comprising a group capable of extending away from the surface of the solid phase, selected from polyalkoxy, polyalkoxylated fatty alcohol, long chain alkyl, polyvinyl alcohol, polyethylene glycol, polyalkoxylated alkyl and polyester;

B is a monomer or a mixture of monomers comprising a group capable of association with the solid phase, selected from sulphonate groups, sulphate groups, either as acids or their corresponding salts or esters, amine groups and silanes; and

C is a monomer or a mixture of monomers other than A and B which is capable of undergoing copolymerisation with A and B;

the molar ratio of n:m being from 100:1 to 1:100 and p being 0 or p being > 0, wherein the molar ratio of (n+m):p is from 100:1 to 1:100.

THE POLYMER

Polymers for use in non-aqueous liquid cleaning products of the invention comprise at least two types of monomer, the first comprising a group, preferably a side-group, which is capable of association with the solid phase, the second comprising a group, preferably a side-group, which is capable of extending away from the surface of the solid phase. In addition to these two monomer types, polymers of the invention may optionally comprise one or more other monomer types.

Generally therefore preferred polymer material for use in products of the invention are random or block copolymers of the general formula:

$$A_n\ B_m\ C_p$$

wherein A is a monomer or a mixture of monomers comprising a group capable of extending away from the surface of the solid phase; B is a monomer or a mixture of monomers comprising a group capable of association with the particulate solid phase of the composition; C is a monomer or a mixture of monomers other than A or B and capable of reacting with A and B, or is absent. The monomers may be randomly distributed or grouped in blocks. As used herein, the term copolymer means a polymer formed from two or

more different monomer types.

In terms of block arrangements, A-B and A-B-A are most preferred although B-$(A)_n$ and -(-A-B$)_n$ can be advantageous. Although possible, B-A-B, $(A\text{-}B)_n$ and -(-B-A$)_n$ are less preferred.

In the above formula, preferably the molar ratio of n : m is preferably from 100 : 1 to 1 : 100, more preferred 50 : 1 to 1 : 50, most preferred 10 : 1 to 1 : 10. Preferably p is 0, i.e. monomer C is absent. If p > 0, then the molar ratio of (n + m) : p is preferably from 100 : 1 to 1 : 100, more preferred, 50 : 1 to 1 : 50, most preferred 5 : 1 to 1 : 30. n and m are each at least 1, for example at least 10.

Preferably the average molecular weight of the polymer material as determined by aqueous gel permeation chromatography using polyacrylate standards is from 500 to 500,000, more preferably from 1,000 to 100,000, and most preferably from 3,000 to 25,000. The determination method is based on aqueous phosphate buffer eluant using Toya Soda and Polymer Laboratories aqueous GPC columns with an ultraviolet detector set at 215 nm.

Polymers for use in compositions according to the invention comprise one or more monomers A having at least one group capable of extending away from the solid phase of the product.

For this purpose it is important that the extending group is predominantly soluble in or at least compatible with the liquid phase of the non-aqueous liquid detergent product of the invention.

Groups for extending away from the surface of the solid phase may be selected from polyalkoxy, polyalkoxylated fatty alcohol, long chain alkyl and polyester.

For example if the liquid phase of the product comprises an alkoxylated fatty alcohol or polyalkoxylated fatty alcohol, a preferred group for extending away from the surface will be a polyalkoxylated C_5-C_{22} fatty alcohol group or a polyalkoxygroup, for example a polyethoxy-, polypropoxy- or polyethoxy/propoxy group. In such groups, the preferred number of alkoxy groups is from 1 to 500, more preferred from 3 to 100, most preferred from 10 to 75. If the liquid phase comprises mainly alkoxylated fatty alcohols then other suitable soluble groups are long-chain alkyl groups for example having C5-20 alkyl groups and groups containing both hydrophobic and polyalkoxy residues, for example those formed by reaction of maleic anhydride with an alkoxylated fatty alcohol.

If, for example the liquid phase of the product comprises another solvent material for example a glyceroltriacetate material, preferred groups for extending away from the surface are polyesters, such as polycaprolactone, phenylmethylmethacrylate, polymethylmethacrylate, polyhydroxypropylacrylate, polyacrylethylester and polyethylmethacrylate groups (as esters and their corresponding acids or salts).

Polymers for use in compositions according to the present invention also comprise a monomer B having at least one group capable of association with the solid phase of the product. Although not wishing to be bound by any theory, the applicants have conjectured that one preferred mechanism of association of the group with the solid phase is caused by direct attachment, for example by an absorption or adsorption process.

Therefore, the group is preferably chosen such that an attractive force exists between the particles of the dispersed solid phase and the group capable of association. This force may either be of a chemical (grafting) or a physical nature, i.e. as determined by the energy of adsorption from solution.

Without wishing to be bound by any theory, one possible mechanism whereby monomer(s) B might become attached to the solid phase could entail adsorption and neutralisation of acid groups on the surface of the solid particles, such that the groups become insoluble. Alternatively, the attractive force may for example be of an electrostatic nature, involving bonding by hydrogen bridges or any other form of polar interaction. Additionally it is preferred that the monomers B are predominantly insoluble in the liquid phase, a feature which contributes to the adsorbtion. A combination of such mechanisms might also be possible.

Preferred association groups are anionic groups such as sulphonate groups, sulphate groups either as acids or their corresponding esters or salts, and other reactive groups such as amine groups and silanes.

In particular, association groups are sulphonate groups (e.g. example 2-acrylamido-2-methyl propane sulphonate or vinyl sulphonate), or sulphate groups, either as acids or their corresponding salts or esters.

The above mentioned groups are especially suitable for use in compositions comprising a liquid phase comprising a liquid nonionic surfactant and a solid phase comprising a bleach material, a bleach activator material and/or a builder material.

The optional filler monomer C is a monomer or a mixture of monomers other than A and B which is capable of undergoing copolymerisation with A and B, or is absent. Monomer C may be any monomer or mixture of monomers capable of reacting with monomers A and B. For example monomers C may be acrylate and methacrylate esters and ethers, ethylene, styrene, unsaturated short chain acids etc. Preferably monomers C comprise unsaturated short chain acids and acrylate and methacrylate esters.

Monomer C can be built in the polymer for environmental reasons. Further the incorporation of the monomer C facilitates easier synthesis and furthermore the synthesis may be made cheaper.

The polymer material can be prepared by conventional polymerisation methods. The resulting polymers may be block polymers, whereby the different monomer units are grouped in one or more blocks, but it is also possible for the different monomers to be randomly distributed over the polymer, as for example those polymers produced by addition free radical polymerisation processes.

Preferably however, the polymers are prepared by polymerising suitable monomers in a substantially non-aqueous liquid medium comprising a detergent and/or an ester of a polyhydric alcohol. Most preferably, if this medium comprises a detergent, then it is a nonionic or cationic liquid detergent. Examples of such nonionic liquid media are polyalkoxylated alcohols. A preferred ester of a polyhydric alcohol is glycerol triacetate (GTA), or other ester of glycerol. The most desirable type of liquid detergent medium chosen for a particular polymerisation reaction will be determined according to a number of considerations, for example the intended eventual formulation of liquid cleaning product.
However, particularly preferred polymerisation media include alcohol ethoxylates of average composition C10 (ethylene oxide) 6 or glycerol triacetate. Preferably, the water content of the medium is no more than 10% by weight, for example less than 5%, preferably less than 3% and most preferably less than 1%.

The polymer material is preferably used in the composition at a level of 0.01 to 10 % by weight, more preferably 0.05 to 8 %, most preferably 0.1 to 3 %.

PRODUCT FORM

All compositions according to the present invention are liquid cleaning products. In the context of this specification, all references to liquid cleaning products refer to those product materials which are liquid at 25°C at atmospheric pressure. They may be formulated in a very wide range of specific forms, according to the intended use. They may be formulated as cleaners for hard surfaces (with or without abrasive) or as agents for warewashing (cleaning of dishes, cutlery etc) either by hand or mechanical means, as well as in the form of specialised cleaning products, such as for surgical apparatus or artificial dentures. Preferably compositions of the invention are formulated as agents for washing and/or conditioning of fabrics.

Thus, the compositions will contain at least one agent which promotes the cleaning and/or conditioning of the article(s) in question, selected according to the intended application. Usually, this agent will be selected from surfactants, enzymes, bleaches, builders, buffers, microbiocides, (for fabrics) fabric softening agents and (in the case of hard surface cleaning) abrasives. Of course in many cases, more than one of these agents will be present, as well as other ingredients commonly used in the relevant product form.

If compositions of the invention are fabric cleaning products they preferably contain a liquid phase containing nonionic surfactants and a solid phase dispersed in the liquid phase, said solid phase comprising one or more of the following ingredients bleaches, bleach activators, builders and solid surfactants. If compositions of the invention are intended for other uses, for example for mechanical warewashing, sometimes the liquid phase will comprise a solvent material other than nonionic surfactant such as for example glyceroltriacetate, paraffin, a low molecular weight polyethylene glycol or an ethoxylated polyethylene glycol. The solid phase of the product will then generally comprise one or more of builders, abrasive materials and solid surfactant materials.

SURFACTANT

Where surfactants are solids, they will usually be dissolved or dispersed in the liquid phase. Where they are liquids, they will usually constitute all or part of the liquid phase. However, in some cases the surfactants may undergo a phase change in the composition.

In general, surfactants for use in the compositions of the invention may be chosen from any of the classes, sub-classes and specific materials described in "Surface Active Agents" Vol. I, by Schwartz & Perry, Interscience 1949 and "Surface Active Agents" Vol. II by Schwartz, Perry & Berch (Interscience 1958), in the current edition of "McCutcheon's Emulsifiers & Detergents" published by the McCutcheon division of Manufacturing Confectioners Company or in "Tensid-Taschenbuch", H. Stache, 2nd Edn., Carl Hanser Verlag, München & Wien, 1981.

NON-IONIC SURFACTANTS

Nonionic detergent surfactants are well-known in the art. They normally consist of a water-solubilizing polyalkoxylene or a mono- or di-alkanolamide group in chemical combination with an organic hydrophobic group derived, for example, from alkylphenols in which the alkyl group contains from about 6 to about 12 carbon atoms, dialkylphenols in which each alkyl group contains from 6 to 12 carbon atoms, primary,

secondary or tertiary aliphatic alcohols (or alkyl-capped derivatives thereof), preferably having from 8 to 20 carbon atoms, monocarboxylic acids having from 10 to about 24 carbon atoms in the alkyl group and polyoxypropylenes. Also common are fatty acid mono- and dialkanolamides in which the alkyl group of the fatty acid radical contains from 10 to about 20 carbon atoms and the alkyloyl group having from 1 to 3 carbon atoms. In any of the mono- and di- alkanolamide derivatives, optionally, there may be a polyoxyalkylene moiety joining the latter groups and the hydrophobic part of the molecule. In all polyalkoxylene containing surfactants, the polyalkoxylene moiety preferably consists of an average of from 2 to 20 groups of ethylene oxide or of ethylene oxide and propylene oxide groups. Amongst the latter class, particularly preferred are those described in the applicants, published European specification EP-A-225,654, especially for use as all or part of the liquid phase. Also preferred are those ethoxylated nonionics which are the condensation products of fatty alcohols with from 9 to 15 carbon atoms condensed with from 3 to 11 moles of ethylene oxide. Examples of these are the condensation products of C11-13 alcohols with (say) 3 to 7 moles of ethylene oxide. These may be used as the sole nonionic surfactants or in combination with those of the described in the last-mentioned European specification, especially as all or part of the liquid phase.

Another class of suitable nonionics comprise the alkyl polysaccharides (polyglycosides/oligosaccharides) such as described in any of specifications US 3,640,998; US 3,346,558; US 4,223,129; EP-A-92,355; EP-A-99,183; EP 70,074, '75, '76, '77; EP 75,994, '95, '96.

Mixtures of different nonionic detergent surfactants may also be used. Especially preferred is the combined use of detergency nonionics with non-detergency nonionics, for example mixtures of alkoxylated fatty alcohols containing 5-10 EO groups and alkoxylated alcohols containing 2-4 EO groups.

Mixtures of nonionic detergent surfactants with other detergent surfactants such as anionic, cationic or ampholytic detergent surfactants and soaps may also be used.

Preferably the level of nonionic surfactants in the composition is from 1 to 90 % by weight, more preferably 5 to 75 %, most preferably 20 to 60 %.

ANIONIC SURFACTANTS

Examples of suitable anionic detergent surfactants are alkali metal, ammonium or alkylolamine salts of alkylbenzene sulphonates or primary alkyl sulphates having from 10 to 18 carbon atoms in the alkyl group, alkyl and alkylether sulphates having from 10 to 24 carbon atoms in the alkyl group, the alkylether sulphates having from 1 to 5 ethylene oxide groups, and olefin sulphonates prepared by sulphonation of C10-24 alpha-olefins and subsequent neutralization and hydrolysis of the sulphonation reaction product and all stable free acid forms of such anionic surfactants.

Compositions of the invention comprise a solid phase dispersed in the liquid phase. As used herein, the term "solids" is to be construed as referring to materials in the solid phase which are added to the composition and are dispersed therein in solid form, those solids which dissolve in the liquid phase and those in the liquid phase which solidify (undergo a phase change) in the composition, wherein they are then dispersed.

THE NON-AQUEOUS ORGANIC SOLVENT

As a general rule, the most suitable liquids to choose as the liquid phase are those organic materials having polar molecules. In particular, those comprising a relatively lipophilic part and a relatively hydrophillic part, especially a hydrophillic part rich in electron lone pairs, tend to be well suited. This is completely in accordance with the observation that liquid surfactants, especially polyalkoxylated nonionics, are one preferred class of material for the liquid phase.

Non-surfactants which are suitable for use as the liquid phase include those having the preferred molecular forms referred to above although other kinds may be used, especially if combined with those of the former, more preferred types. In general, the non-surfactant solvents can be used alone or with in combination with liquid surfactants. Non-surfactant solvents which have molecular structures which fall into the former, more preferred category include ethers, polyethers, alkylamines and fatty amines, (especially di- and tri-alkyl- and/or fatty-N-substituted amines), alkyl (or fatty) amides and mono- and di-N-alkyl substituted derivatives thereof, alkyl (or fatty) carboxylic acid lower alkyl esters, ketones, aldehydes, and glycerides. Specific examples include respectively, di-alkyl ethers, polyethylene glycols, alkyl ketones (such as acetone) and glyceryl trialkylcarboxylates (such as glyceryl triacetate, hereinafter referred to as GTA), glycerol, propylene glycol, and sorbitol.

Many light solvents with little or no hydrophillic character are in most systems, to a small extent, unsuitable on their own. Examples of these are lower alcohols, such as ethanol, or higher alcohols, such as

dodecanol, as well as alkanes and olefins. However, they can be combined with other liquid materials.

PROPORTION OF LIQUID PHASE

Preferably, the compositions of the invention contain the liquid phase (whether or not comprising liquid surfactant) in an amount of at least 10% by weight of the total composition. The amount of the liquid phase present in the composition may be as high as about 90%, but in most cases the practical amount will lie between 20 and 70% and preferably between 35 and 60% by weight of the composition.

SOLIDS CONTENT

In general, the solids content of the product may be within a very wide range, for example from 10-90%, usually from 30-80% and preferably from 40-65% by weight of the final composition. The solid phase should be in particulate form and have a weight average particle size of less than 300 microns, preferably less than 200 microns, more preferably less than 100 microns, especially less than 10 microns. The particle size may even be of sub-micron size. The proper particle size can be obtained by using materials of the appropriate size or by milling the total product in a suitable milling apparatus. In order to control aggregation of the solid phase leading to unredispersible settling or setting of the composition, it is preferred to include a deflocculant therein.

OTHER INGREDIENTS

In addition to the components already discussed, there are very many other ingredients which can be incorporated in liquid cleaning products.

There is a very great range of such other ingredients and these will be choosen according to the intended use of the product. However, the greatest diversity is found in products for fabrics washing and/or conditioning. Many ingredients intended for that purpose will also find application in products for other applications (e.g. in hard surface cleaners and warewashing liquids).

HYDROPHOBICALLY MODIFIED MATERIALS

Surprisingly, it has been found that the physical stability of non-aqueous liquid detergent compositions can be even further improved and/or setting problems can be minimised, if hydrophobically modified dispersants (hereinafter termed HM materials) are used. For the purpose of the present invention, a dispersant material is a material, of which the main purpose is to stabilise the composition.
Hydrophobically modified dispersant materials are particulate materials, of which the outer surface has chemically been treated to reduce the hydrophillic nature thereof.

Preferred HM materials have a weight average particle size of from 0.005 to 5 micrometers, more preferred 0.01 to 3 micrometers, most preferred from 0.02 to 0.5 micrometer. The amount of the HM material is preferably from 0.1 to 10 % by weight of the composition, more preferred 0.3 to 5 %, most preferred from 0.5 to 3 %.

Preferably the number of hydroxy- and/or acid- groups at the surface of the particles is reduced by the hydrophobic modification treatment. Suitable reactions include esterification or etherification of the hydrophillic groups. Preferably the hydrophobic modification treatment involves at least 10 % of the hydrophillic groups at the surface of the particle, more preferably from 40 to 95 %, most preferably from 50 to 90 %. Partial hydrophobing is preferred over complete hydrophobic modification.

Preferably HM silica containing dispersants are used. The hydrophobic modification of the silica particles preferably involves the substitution of the free hydroxy-groups at the outer surface of the silica particles by a short alkyl or silyl group. More preferably the surface hydroxy-groups are substituted by methyl groups.

For even greater reduction the clear layer separation of liquid detergent compositions of the invention, it has been found that the use of particulate metal oxides is especially advantageous. Preferred suspended metal oxides have a bulk density of 200 to 1,000 g/l, more preferred 250 to 800 g/l, especially preferably 300 to 700 g/l, most preferably from 400 to 650 g/l.

Preferably, the metal oxide is selected from calcium oxide, magnesium oxide and aluminium oxide, most preferably magnesium oxide is used.

The weight average particle size of the metal oxide is preferably from 0.1 to 200 micrometers, more preferably from 0.5 to 100 micrometers, most preferably from 2 to 70 micrometers. The level of metal oxide

is preferably from 0.1 to 7 % by weight of the composition, more preferably from 0.5 to 5 %, most preferably from 1 to 4 %.

DETERGENCY BUILDERS

The detergency builders are those materials which counteract the effects of calcium, or other ion, water hardness, either by precipitation or by an ion sequestering effect. They comprise both inorganic and organic builders. They may also be sub-divided into the phosphorus-containing and non-phosphorus types, the latter being preferred when environmental considerations are important.

In general, the inorganic builders comprise the various phosphate-, carbonate-, silicate-, borate- and aluminosilicates-type materials, particularly the alkali-metal salt forms. Mixtures of these may also be used.

Examples of phosphorus-containing inorganic builders, when present, include the water-soluble salts, especially alkali metal pyrophosphates, orthophosphates, polyphosphates and phosphonates. Specific examples of inorganic phosphate builders include sodium and potassium tripolyphosphates, phosphates and hexametaphosphates.

Examples of non-phosphorus-containing inorganic builders, when present, include water-soluble alkali metal carbonates, bicarbonates, borates, silicates, metasilicates, and crystalline and amorphous aluminosilicates. Specific examples include sodium carbonate (with or without calcite seeds), potassium carbonate, sodium and potassium bicarbonates, silicates and zeolites.

Examples of organic builders include the alkali metal, ammonium and substituted ammonium, citrates, succinates, malonates, fatty acid sulphonates, carboxymethoxy succinates, ammonium polyacetates, carboxylates, polycarboxylates, aminopolycarboxylates, polyacetyl carboxylates and polyhydroxysulphonates. Specific examples include sodium, potassium, lithium, ammonium and substituted ammonium salts of ethylenediaminetetraacetic acid, nitrilotriacetic acid, oxydisuccinic acid, melitic acid, benzene polycarboxylic acids and citric acid. Other examples are organic phosphonate type sequestering agents such as those sold by Monsanto under the tradename of the Dequest range and alkanehydroxy phosphonates.

Other suitable organic builders include the higher molecular weight polymers and copolymers known to have builder properties, for example appropriate polyacrylic acid, polymaleic acid and polyacrylic/ polymaleic acid copolymers and their salts, such as those sold by BASF under the Sokalan Trade Mark. Preferably the level of builder materials is from 0-60%, more preferred 5-50%, most preferred 10-40% by weight.

THE DEFLOCCULANT

Preferably compositions of the invention also comprise one or more deflocculant materials. In principle, any material may be used as a deflocculant provided it fulfils the deflocculation test described in European Patent Specification EP-A-266 199 (Unilever). The capability of a substance to act as a deflocculant will partly depend on the solids/liquid phase combination. However, especially preferred are acids.

Some typical examples of deflocculants include the alkanoic acids such as acetic, propionic and stearic acids and their halogenated counterparts such as trichloracetic and trifluoracetic as well as the alkyl (e.g. methane) sulphonic acids and aralkyl (e.g. paratoluene) sulphonic acids.

Examples of suitable inorganic mineral acids and their salts are hydrochloric, carbonic, sulphurous, sulphuric and phosphoric acids; potassium monohydrogen sulphate, sodium monohydrogen sulphate, potassium monohydrogen phosphate, potassium dihydrogen phosphate, sodium monohydrogen phosphate, potassium dihydrogen pyrophosphate, tetrasodium monohydrogen triphosphate.

Other organic acids may also be used as deflocculants, for example formic, lactic, amino acetic, benzoic, salicylic, phthalic, nicotinic, ascorbic, ethylenediamine tetraacetic, and aminophosphonic acids, as well as longer chain fatty carboxylates and triglycerides, such as oleic, stearic, lauric acid and the like. Peracids such as percarboxylic and persulphonic acids may also be used.

The class of acid deflocculants further extends to the Lewis acids, including the anhydrides of inorganic and organic acids. Examples of these are acetic anhydride, maleic anhydride, phthalic anhydride and succinic anhydride, sulphur-trioxide, diphosphorous pentoxide, boron trifluoride, antimony pentachloride.

"Fatty" anions are very suitable deflocculants, and a particularly preferred class of deflocculants comprises anionic surfactants. Although anionics which are salts of alkali or other metals may be used, particularly preferred are the free acid forms of these surfactants (wherein the metal cation is replaced by an $H+$ cation, i.e. proton). These anionic surfactants include all those classes, sub-classes and specific forms described in the aforementioned general references on surfactants, viz, Schwartz & Perry, Schwartz Perry and Berch, McCutcheon's, Tensid-Taschenbuch; and the free acid forms of such surfactants. Many

anionic surfactants have already been described hereinbefore. In the role of deflocculants, the free acid forms of these are generally preferred.

In particular, some preferred sub-classes and examples are the C10-C22 fatty acids and dimers thereof, the C8-C18 alkylbenzene sulphonic acids, the C10-C18 alkyl or alkylether sulphuric acid monoesters, the C12-C18 paraffin sulphonic acids, the fatty acid sulphonic acids, the benzene-, toluene-, xylene- and cumene sulphonic acids and so on. Particularly preferred are the linear C12-C18 alkylbenzene sulphonic acids.

As well as anionic surfactants, zwitterionic-types can also be used as deflocculants. These may be any described in the aforementioned general surfactant references. one example is lecithin.

The level of the deflocculant material in the composition can be optimised by the means described in the aforementioned EP-A-266 199, but in very many cases is at least 0.01%, usually 0.1% and preferably at least 1% by weight, and may be as high as 15% by weight. For most practical purposes, the amount ranges from 2-12%, preferably from 4-10% by weight, based on the final composition. Surprisingly, however it has been found that for obtaining stability, in compositions of the invention generally the presence of the polymer material reduces the need for high levels of deflocculant material.

THE BLEACH SYSTEM

Bleaches include the halogen, particularly chlorine bleaches such as are provided in the form of alkalimetal hypohalites, e.g. hypochlorites. In the application of fabrics washing, the oxygen bleaches are preferred, for example in the form of an inorganic persalt, preferably with a bleach precursor, or as a peroxy acid compound.

In the case of the inorganic persalt bleaches, the activator makes the bleaching more effective at lower temperatures, i.e. in the range from ambient temperature to about 60 °C, so that such bleach systems are commonly known as low-temperature bleach systems and are well-known in the art. The inorganic persalt such as sodium perborate, both the monohydrate and the tetrahydrate, acts to release active oxygen in solution, and the activator is usually an organic compound having one or more reactive acyl residues, which cause the formation of peracids, the latter providing for a more effective bleaching action at lower temperatures than the peroxybleach compound alone. The ratio by weight of the peroxybleach compound to the activator is from about 20:1 to about 2:1, preferably from about 10:1 to about 3.5:1. Whilst the amount of the bleach system, i.e. peroxybleach compound and activator, may be varied between about 5% and about 35% by weight of the total liquid, it is preferred to use from about 6% to about 30% of the ingredients forming the bleach system. Thus, the preferred level of the peroxybleach compound in the composition is between about 5.5% and about 27% by weight, while the preferred level of the activator is between about 0.5% and about 14%, most preferably between about 1% and about 7% by weight.

Typical examples of the suitable peroxybleach compounds are alkalimetal perborates, both tetrahydrates and monohydrates, alkali metal percarbonates, persilicates and perphosphates, of which sodium perborate is preferred.

It is particularly preferred to include in the compositions, a stabiliser for the bleach or bleach system, for example ethylene diamine tetramethylene phosphonate and diethylene triamine pentamethylene phosphonate or other appropriate organic phosphonate or salt thereof, such as the Dequest range hereinbefore described. These stabilisers can be used in acid or salt form, such as the calcium, magnesium, zinc or aluminium salt form. The stabiliser may be present at a level of up to about 1% by weight, preferably between about 0.1% and about 0.5% by weight.

The applicants have also found that liquid bleach precursors, such as glycerol triacetate and ethylidene heptanoate acetate, isopropenyl acetate and the like, also function suitably as a material for the liquid phase, thus obviating or reducing any need of additional relatively volatile solvents, such as the lower alkanols, paraffins, glycols and glycolethers and the like, e.g. for viscosity control.

MISCELLANEOUS OTHER INGREDIENTS

Other ingredients comprise those remaining ingredients which may be used in liquid cleaning products, such as fabric conditioning agents, enzymes, perfumes (including deoperfumes), micro-biocides, colouring agents, fluorescers, soil-suspending agents (anti-redeposition agents), corrosion inhibitors, enzyme stabilising agents, and lather depressants.

Amongst the fabric conditioning agents which may be used, either in fabric washing liquids or in rinse conditioners, are fabric softening materials such as fabric softening clays, quaternary ammonium salts, imidazolinium salts, fatty amines and cellulases. Enzymes which can be used in liquids according to the

present invention include proteolytic enzymes, amylolytic enzymes and lipolytic enzymes (lipases). Various types of proteolytic enzymes and amylolytic enzymes are known in the art and are commercially available. They may be incorporated as "prills", "marumes" or suspensions.

The fluorescent agents which can be used in the liquid cleaning products according to the invention are well known and many such fluorescent agents are available commercially. Usually, these fluorescent agents are supplied and used in the form of their alkali metal salts, for example, the sodium salts. The total amount of the fluorescent agent or agents used in a detergent composition is generally from 0.02-2% by weight.

When it is desired to include anti-redeposition agents in the liquid cleaning products, the amount thereof is normally from about 0.1% to about 5% by weight, preferably from about 0.2% to about 2.5% by weight of the total liquid composition. Preferred anti-redeposition agents include carboxy derivatives of sugars and celluloses, e.g. sodium carboxymethyl cellulose, anionic polyelectrolytes, especially polymeric aliphatic carboxylates, or organic phosphonates.

WATER

The compositions are substantially non-aqueous, i.e. they contain little or no free water, preferably no more than 5%, preferably less than 3%, especially less than 1% by weight of the total composition. It has been found that the higher the water content, the more likely it is for the viscosity to be too high, or even for setting to occur.

USE

Composition in accordance with the present invention may be used for several detergency purposes, for example the cleaning of surfaces and the washing of fabrics. For the washing of fabrics, preferably an aqueous liquor containing 0.1 to 10 %, more preferably 0.2 to 2%, of the non-aqueous detergent composition of the invention is used.

PROCESSING

During manufacture, it is preferred that all raw materials should be dry and (in the case of hydratable salts) in a low hydration state, e.g. anhydrous phosphate builder, sodium perborate monohydrate and dry calcite abrasive, where these are employed in the composition. In a preferred process, the dry, substantially anhydrous solids are blended with the liquid phase in a dry vessel. If deflocculant materials are used, these should preferably -at least partly- be mixed with the liquid phase, prior to the addition of the solids. In order to minimise the rate of sedimentation of the solids, this blend is passed through a grinding mill or a combination of mills, e.g. a colloid mill, a corundum disc mill, a horizontal or vertical agitated ball mill, to achieve a particle size of 0.1 to 100 microns, preferably 0.5 to 50 microns, ideally 1 to 10 microns. A preferred combination of such mills is a colloid mill followed by a horizontal ball mill since these can be operated under the conditions required to provide a narrow size distribution in the final product. Of course particulate material already having the desired particle size need not be subjected to this procedure and if desired, can be incorporated during a later stage of processing.

During this milling procedure, the energy input results in a temperature rise in the product and the liberation of air entrapped in or between the particles of the solid ingredients. It is therefore highly desirable to mix any heat sensitive ingredients into the product after the milling stage and a subsequent cooling step. It may also be desirable to de-aerate the product before addition of these (usually minor) ingredients and optionally, at any other stage of the process. Typical ingredients which might be added at this stage are perfumes and enzymes, but might also include highly temperature sensitive bleach components or volatile solvent components which may be desirable in the final composition. However, it is especially preferred that volatile material be introduced after any step of de-aeration. Suitable equipment for cooling (e.g. heat exchangers) and de-aeration will be known to those skilled in the art.

It follows that all equipment used in this process should preferably be completely dry, special care being taken after any cleaning operations. The same is true for subsequent storage and packing equipment.

Example I

The following basic formulation was prepared by mixing the ingredients in the order listed, followed by milling to a weight average particle size of 5 μm.

Basic product	Parts by weight:
Vista® 1012-62 (1)	23.8
Synperonic® A3 (2)	19.5
GTA	5.0
Marlon® AS 3 (3)	6.0
Anti-foam	1.0
Sodium carbonate	18.0
Socal® U 3 (4)	7.0
SCMC	1.0
Versa® TL 3 (5)	1.0
Fluorescer	0.1
Sipernat® D 17 (6)	3.0
Perborate mono.	10.5
TAED	3.0
Minors	1.1

(1) Narrow range ethoxylated nonionic ex Vista
(2) C_{13-15} alcohol alkoxylated with on average 3 EO groups ex ICI
(3) Anionic detergent in acid form ex Huls
(4) High surface area calcium carbonate
(5) Copolymer of sulphonated styrene and maleic anhydride, Na salt, ex National Starch & Chemical Co.
(6) Hydrophobically modified silica dispersant ex Degussa

On top of the formulation the following ingredients were added:

Composition	A	B	C	D	E
Dobanol 91-6®(7)	2.3	2.8	5.7	5.7	-
Polymer	-	0.5	-	0.5	1.0

(7) ethoxylated nonionic ex Shell

The following polymers were prepared by randomly copolymerising the following monomers in the stated weight ratios:

Weight Percentage:-						
Polymer	MW	AA	MMA	AMPS	Extending Group	Extending Group type
Al	12000	64		1	35	Lauryl methacrylate
A2	12000	55		10	35	Lauryl methacrylate
A3	12000		70	20	10	Lauryl methacrylate
A4	12000		45	20	35	Lauryl methacrylate
A5	12000	70		20	10	Lauryl methacrylate
A6	12000	45		20	35	Lauryl methacrylate
A7	12000	60		20	20	Lauryl methacrylate
A8	12000	65		20	15	Lauryl methacrylate
A9	15500	65		20	16	Dobanol 91-6 maleate half ester
A10	9100	65		20	15	Vista 1012-62 maleate half ester
All9250		66.7		22.3	11	PEG350MA
A128500		52.5		22	25.5	PEG1000MA
A138550		38.6		22.5	38.9	Allyl 44EO
A148150		38.6		22.5	38.9	PEG2000MA

AA = acrylic acid = monomer C
MMA = methyl methacrylate = monomer C
AMPS = 2-acrylamido-2-methyl propane sulphonic acid = monomer B
Extending Group = as indicated, wherein:
PEG refers to polyethylene glycol, the PEG unit refers to the average molecular weight, MA refers to methacrylate esters,
and EO refers to ethylene oxide units = monomer A.

The initial viscosity of the products was measured at 21 s^{-1} in mPa.s. The products were stored for 4-8 weeks at 37° C and the formation of a clear layer was measured in mm.

The following results were obtained

Basic formulations	viscosity			Clear Layer Separation
	Polymer	mPa.s	4 weeks	8 weeks
B	Al	985	2.0	2.0
B	A2	512	2.0	3.0
B	A3	560	2.5	3.0
B	A4	615	<3.0	3.5
B	A5	520	2.0	2.5
B	A6	573	2.5	3.0
B	A7	510	2.5	3.0
B	A8	517	2.5	3.0
B	A9	575	3.0	4.5
A		677	4.5	7.0
D	Al	1130	1.5	2.0
D	A2	470	2.0	3.0*
D	A3	533	2.0	2.5+
D	A4	580	2.5	2.5+
D	A5	505	6.0	8.5*+
D	A6	505	2.5	3.5
D	A7	460	2.5	2.5+
D	A8	470	2.0	2.0+
D	A9	500	3.0	4.0
C	-	560	8.0	11.0

* The upper layer was not clear 2 layers
+ 2 layers

The results clearly indicate that the inclusion of polymers according to the invention clearly reduces the clear layer separation.

Example II

The following formulations (parts by weight) were made by mixing the ingredients in the order listed. After addition of the TAED, the compositions were ball-milled to a weight average particle size of 5µm whereafter the remaining ingredients were post-dosed. The initial viscosity of the formulations was measured in mPa.s at 21 s-1 and the clear layer formation was measured in mm after 4 weeks, storage at 20°C. The following results were obtained:

Ingredient (parts by weight)

Formulation:	A	B	C	D	E	F	G	H
Vista® 1012-62	<----------------23.0------------------>							
Synperonic® A3	<----------------19.0------------------>							
GTA	<-----------------5.0------------------>							
Marlon® AS3	6.0	6.0	5.0	4.0	3.0	2.0	1.0	0.5
Polymer A 10	-	0.5	0.5	0.5	0.5	0.5	0.5	0.5
Antifoam	<-----------------1.0------------------>							
Sodium carbonate	<----------------18.8------------------>							
Socal® U3 (Calcite)	<-----------------6.0------------------>							
SCMC	<-----------------1.5------------------>							
Versa® TL 3	<-----------------1.5------------------>							
Fluorescer	<-----------------0.1------------------>							
Sipernat® D 17	<-----------------3.0------------------>							
Perborate mono.	<----------------10.5------------------>							
TAED	<-----------------3.0------------------>							
Minor ingredients	<-----------------1.1------------------>							
Total	99.5	100.0	99.0	98.0	97.0	96.0	95.0	94.5

The only difference between formulations B-H is the amount of Marlon AS3. Polymer A10 was as above, prepared as a 20% solution in Vista® 1012-62.

Results

Formulation:		A	B	C	D	E	F	G	H
Initial viscosity		1140	876	804	780	756	672	660	660
Specific Gravity		1.298	1.301	1.305	1.308	1.311	1.314	1.318	1.320
Clear Layer Separation (mm)									
20°C	4 weeks	2.0	<2.0	<2.0	1.5	<2.0	1.5	1.5	1.5
	8 weeks	2.0	2.0	2.0	2.0	1.5	1.5	1.5b	1.5b
37°C	4 weeks	<4.0	3.0	2.5	<2.0B	1.5*	1.0*	<1.0*	1.0*
	8 weeks	6.5	4.0a	3.0b	2.5*				

Note *100% set, no further measurements
a 15% set
b 50% set
B bottom layer remaining on pouring out

To determine to what extent the polymer A10 can act as an anti-redeposition and anti-ashing agent, an appraisal was carried out with a product prepared as formulation H in Example II but with the amount of polymer A10 raised to 1.0% (the new formulation hereafter being call H'). The latter was tested for % ash deposition in comparison with the 'Basic Product' referred to in Example I. This results (tabulated below) in effect show a very favourable performance for polymer A10 in place of the standard anti-ashing polymer Versa® TL3 used in the Basic Product.

Results:

		Basic Product	H'
40°C		%	%
Cotton:	5 washes	0.6	0.4
Polyester:	5 washes	0.2	0.1
60°C			
Cotton:	5 washes	0.6	0.4
	10 washes	-	0.5
Polyester:	5 washes	-	0.2
	10 washes	-	0.2

The results indicate that low levels of such polymers in compositions of the invention allow a reduction of the level of deflocculant material (Marlon® AS 3) while not adversely affecting clear layer separation. Furthermore, subsidiary benefits such as anti-ashing may be obtained in some cases.

Example III

The following formulation (parts by weight) was prepared by mixing the ingredients in the listed order. After addition of the perborate, the formulation was milled to a weight average particle size of 5μm, whereafter the remaining ingredients were added.

Ingredient	wt. parts
Vista ® 1012-62	23.0
Synperonic® A3	19.0
Marlon® AS 3	0.5
Anti foam	1.0
Sodium carbonate	18.8
Socal U3® (Calcite)	6.0
Versa® TL 3	1.5
SCMC	1.5
Fluorescer	0.1
Sipernat® D 17	3.0
TAED	3.0
Perborate mono.	10.5
GTA	5.0
Minor ingredients	1.1

The polymers were added on top as a 20% solution in Vista® 1012-62. Percentages of polymer refer to 100% active.

The viscosity of the product was measured at 21 s^{-1} (mPa.s.). The following results were obtained:

Polymer level % wt.	0	0.05	0.1	0.25	0.5	1
Polymer	948	-	-	-	-	-
A10	-	912	948	816	672	576
All	-	960	972	852	732	636
A12	-	960	936	912	840	756
A13	-	936	924	960	864	768
A14	-	948	900	840	720	660

These results clearly indicate that a reduction of viscosity can be obtained by adding polymers according to the invention to non-aqueous cleaning liquids.

Example IV

A basic formulation according to Example III was prepared containing various levels of polymer A 14. The setting and the clear layer separation were measured. The clear layer separation (CLS) is measured in mm. The setting % refers to the weight % of product which did not pour when the bottle was placed on its side and left for one minute.

The following results were obtained:

Level of polymer	CLS					
	0	0.05	0.1	0.25	0.5	1.0.
Storage time						
4 weeks 20°C	2.5	2.5	2.5	2.0	<2.0	1.5
8 weeks 20°C	3.5	3.5	3.0	2.0	2.0	2.0
4 weeks 37°C	2.5	<4.0	4.0	<3.75	3.0	2.0
8 weeks 37°C	-	3.0	3.5	2.5	2.5	2.0
4 weeks 20°C	0	0	0	0	0	0
8 weeks 20°C	0	0	0	0	0	0
4 weeks 37°C	100	90	90	75	B	B
8 weeks 37°C	100	75	100	25	B	B
B indicates that, upon pouring, a bottom layer larger than normal remained in the bottle.						

These results indicate that by storage at 20°C an improvement in reduction of clear layer separation could be obtained, without the occurrence of setting. At 37°C some increases in clear layer separation were observed, but an advantageous reduction of setting occurred.

Example V

The following formulations (parts by weight) were made by mixing the ingredients in the listed order. After addition of the perborate and the polymer, the compositions were milled to a weight average particle size of 5μm. The TAED was added to the product just before testing.

INGREDIENT	Basic product	Polymer product
	Parts by weight	
Vista® 1012-62	23.8	23.8
Marlon® AS 3	6.0	0.5
Sodium carbonate	18.0	18.0
Synperonic® A3	19.5	19.5
Antifoam	1.0	1.0
Socal® U3	7.0	7.0
Versa® TL 3	1.0	-
SCMC	1.0	1.0
Fluorescer	0.1	0.1
Sipernat® D 17	3.0	3.0
Perborate mono.	10.5	10.5
Polymer A 14	-	1.0
GTA	5.0	5.0
Minor ingr.	1.2	1.2
TAED*	3.0	3.0
Total	100.0	94.5
Viscosity (mPa.s at $21/s^{-1}$) before addition of TAED	1008	480

The performance of the products was tested at 40 °C in a Philips 1200 Silent 77 AWG. The dosage for the basic product was 90 ml, for the polymer product 85 ml. The performance was measured by determining the Reflectance Value Delta R 460.

The following results were obtained:

Stain	Delta R 460 basic product	Delta R 460 polymer product
AS 9	16	17
WFK 10 C	11	12
WFK 20 C	14	17.5
WFK 30 C	11	11
EM-104	14	20
AS 10	29	29
BC 1	7.5	7.5
EM 114	19	20
Gravy	45	44
Cooking oil	15	15
Clay/oil	41	44
Lipstick	13	16
Make-up	30	36
Dirty motor oil	15	15
Cocoa	2	8
Blackcurrant	20	20

The first eight stains are standards known to those skilled in the art.

These results indicate that replacement of Versa® TL polyacrylate by a polymer of the invention allows a significant reduction of the anionic material; still, on average, the washing performance of the product is better than that of the comparative basic product.

Example VI

The following compositions were made by mixing the ingredients in the listed order. After addition of the MgO, the sample was stirred for 20 minutes. After mixing, the samples were milled to a surface volume (D3,2) mean diameter of about 8 µm.

Ingredient	Parts
Vista ® Novel 1012-62	42
GTA	5
Marlon® AS 3	4
MgO (bulk density 170 g/l)	0.2
Carbonate	24.2
Calcite	5
Perborate mono	13.1
TAED	4
SCMC	1
Versa® TL-3	0.5
Minors	1

The polymer, if added, was used on top of the other components as a pre-solution in the nonionic. Percentages of polymer refer to 100% active.

Polymer A (comparison) was a polyethylene oxide having a molecular weight of about 14,000. Polymer B (comparison) was a poly (2-vinyl pyridine carboxylate sodium salt) having a molecular weight of 5,000. Polymer C (invention) was a block co-polymer ABA comprising sequential blocks of polyethylene oxide polymer A, poly(2-vinyl pyridine carboxylate sodium salt) polymer B and polyethylene oxide polymer A, prepared by a method similar to those described in S. Billmeyer, "Textbook of Polymer Science", Wiley Interscience, 1987.

The clear layer separation (CLS) of the formulations was measured as in the previous Examples after 8 weeks' storage at 37°C. The following results were obtained:

Polymer type	polymer level % wt.	CLS mm	Viscosity (mPas) at $21s^{-1}$, 25°C after 8 weeks
None	-	14	956
A	0.125	13	1860
A	0.25	13	1750
B	0.125	13.5	1310
B	0.25	12.5	1380
ABA	0.125	10	1100
ABA	0.25	11	1015

These results indicate that reduction in clear layer formation can be observed by using a polymer ABA.

Example VII

The following formulations were prepared by first weighing and mixing the solid materials and subsequently mixing the ingredients to the GTA. Finally, the polymer was added to the dispersions. The product was homogenised and the particle size was reduced to d 3,2 average of 15µm by milling.

Ingredient	dry mix (parts by weight)
Citrate	49.3
Sokalan® CP 5	11.0
Disilicate monohydrate	20.1
Perborate mono	11.8
TAED	5.1
Dequest	1.75
Polymer	0/0.5

35 volume parts of the dry mix were used in combination with 65 weight parts of GTA.

The consistency of the product was measured in Pa at levels of polymer of 0 and 0.5 using a Carri-Med CS rheometer with a concentric cylinder system comprising a ribbed bob with a tip radius of 8.6 mm and a

cup with a radius of 9.33 mm. The viscosities were measured in a sweep mode while the shear rates varied from 0 to about 400 s^{-1}. The consistencies were determined by a fit procedure on the "down" curve using the Sisko equation in Pa at polymer levels of 0 to 0.5%. The following results were obtained:

Polymer	level	Consistency (Pa)
-	-	9.1
B1	0.5	5.0
B2	0.5	5.0
B3	0.5	3.0

Weight Percentage:-

Polymer	BA	MMA	HPA	A172	Extending Group	Extending Group Type
B1	10	68	0	2	20	lauryl methacrylate
B2	48	40	0	2	10	" "
B3	48	0	40	2	10	" "

Definitions:

BA = butyl acrylate = monomer C
HPA = hydroxypropyl acrylate = monomer C
MMA = methyl methacrylate = monomer C
Lauryl methacrylate = monomer A
A172 = vinyl-tris-(2-methoxyethoxy) silane obtainable from Union Carbide = monomer B

These results clearly indicate that a surprising reduction in consistency can be obtained by using polymer according to the invention.

Example VIII

The following formulations were prepared as indicated in Example VII. The particle size after milling was reduced to a $d_{2,3}$ average of 15 - 19 µm. 35 volume parts of the dry mix, as indicated in the table in the same example were used in combination with 65 volume parts of Plurafac RA30 nonionic. The following polymers were used:

Weight Percentage:-

Polymer	AA	MMA	HPA	AMPS	Extending Group	Extending Group Type
C1	0	0	80	10	10	Lauryl methacrylate
C2	45	0	0	20	35	,, ,,
C3	0	45	0	20	35	,, ,,
C4	0	80	0	10	10	,, ,,
C5	80	0	0	10	10	,, ,,
C6	0	90	0	10	10	0
C7	0	80	0	10	10	Stearyl methacrylate
C8	0	80	0	10	10	PEG 350 MA
C9	0	80	0	10	10	PEG 2000 MA

AA = Acrylic acid = monomer C
MMA = Methyl methacrylate = " "
HPA = Hydroxy propyl acrylate = " "
AMPS = 2-acrylamido-2-methyl propane sulphonic acid = monomer B
Extending Group = as indicated wherein PEG refers to polyethylene glycol. MA refers to methacrylate esters, PEG unit refers to average molecular weight = monomer A.

The consistencies of these products were measured according to the method described in Example VII.

Polymer	level (%)	Consistency(Pa)
-	0	32.59
C1	0.2	0.103
C2	0.2	0.098
C3	0.2	0.173
C4	0.2	0
C5	0.2	5.331
C6	0.2	1.546
C7	0.2	0
C8	0.2	2.796
C9	0.2	-

EXAMPLE IX

The basic formulation of Example I (composition E) was used. The viscosity of the basic product was measured, as well as the viscosity of the basic product with 1% by weight of a polymer. The viscosity was measured at shear rates of 2.5, 20 and 80 s^{-1}.

The following results were obtained:

Polymer	Viscosity (mPa.s) measured at a shear rate (s-1) of 2.5	20	80
-	971	381	260
A-B polymer 1)	544	208	161
Sokalan® CP5	1073	412	315
Polyacrylate 2)	1100	450	335
Gantrez® AN-119 Methyl half ester	962	384	285

1) 50-50% by weight copolymer AMPS/PEG1000MA, wherein:
AMPS = 2-acrylamido-2-methyl propane sulphonic acid = monomer B
PEG refers to polyethylene glycol, the PEG unit refers to the average molecular weight; MA refers to methacrylate esters = monomer A.

2) The molecular weight is 50,000

3) Measured with a Haake VT 181 viscometer at 25°C

The above data show that the A-B polymer, according to the invention, results in lower viscosity than the polymers of the art.

Claims

1. A non-aqueous liquid cleaning composition comprising a particulate solid phase which is dispersed in a non-aqueous liquid phase, and a polymer, wherein the polymer is a random or block copolymer having the general formula:

   $A_nB_mC_p$

   wherein:

A is a monomer or a mixture of monomers comprising a group capable of extending away from the surface of the solid phase, selected from polyalkoxy, polyalkoxylated fatty alcohol, long chain alkyl and polyester;

B is a monomer or a mixture of monomers comprising a group capable of association with the solid phase, selected from sulphonate groups, sulphate groups, either as acids or their corresponding salts or esters, amine groups and silane; and

C is a monomer or a mixture of monomers other than A and B which is capable of undergoing copolymerisation with A and B, or is absent;

the molar ratio of n:m being from 100:1 to 1:100 and p being 0 or p being > 0, wherein the molar ratio of (n + m):p is from 100:1 to 1:100.

2. A composition according to claim 1 characterised in that the polymer has a molecular weight of 500 to 500,000.

3. A composition according to claim 1 characterised in that the polymer has a molecular weight of 1,000 to 100,000.

4. A composition according to claims 1-3 characterised in that the molar ratio of n:m is from 50:1 to 1:50.

5. A composition according to claims 1-4 characterised in that the molar ratio of (n + m):p is from 50:1 to 1:50.

6. A composition according to claims 1-5 characterised in that the monomer B comprises sulphonate groups or sulphate groups, either as acids or their corresponding salts or esters.

7. A composition according to claims 1-6 characterised in that the amount of the polymer material, or the copolymer, as appropriate, is from 0.01% to 10% by weight of the total composition.